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(54) **PAPERMAKING PROCESS**

(57) There is provided a papermaking method which comprises the steps of adding to pulp in a paper-making step an ionic water-soluble polymer produced by a polymerization method for obtaining a dispersion of fine polymer particles by carrying out polymerization under agitation in an aqueous salt solution capable of dissolving monomers but not the produced polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous salt solution and then adding an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof so as to improve retention and/or drainage property. The present invention makes it possible to greatly improve the retention and drainage property of paper stuff and fillers in the paper-making process and thereby enhance quality and productivity.

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Description

TECHNICAL FIELD

5 This invention relates to a papermaking method in a papermaking process and, more specifically, to a papermaking method for improving retention and/or drainage property by adding an ionic water-soluble polymer prepared by a specific production method and an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof to pulp in a papermaking step.

10 BACKGROUND ART

Heretofore, the papermaking step has involved such a problem that a composition distribution in the direction of the thickness of a paper layer becomes nonuniform due to the effluence of various added fillers. There have also been such problems to be solved that cost is increased by the effluence of paper stuff and added chemicals and that the concentration of the paper stuff needs to be more than a predetermined value. The effluence of the fillers and the like causes the contamination of circulating white water. To solve these problems, a certain kind of retention aid is added.

15 Furthermore, an increase in the papermaking speed during papermaking leads to improvement of productivity whereas the increasing of the beating degree of pulp, which is desired from a view point of increasing paper strength, is contradictory to the papermaking speed. Therefore, it has been difficult to solve these at the same time. To solve the problem, a drainage aid is added.

20 As the retention aid or drainage aid is generally used a water-soluble polymeric substance, namely, a synthetic polymeric substance such as polyacrylamide or a derivative thereof, polyethylene-imine or polyamide polyamine epichlorohydrin resin, or a natural water-soluble polymeric substance such as starch or a derivative thereof.

For the purpose of further improving retention and/or drainage property, various methods have been proposed. 25 They include one in which colloid silica is added to paper stuff for making paper after cationic or amphoteric water-soluble polymer is added (Laid-open Japanese Patent Application No. Hei 3-27676), one in which cationic starch or Hoffman reaction product of polyacrylamide is added to paper stuff after anionic acrylamide-based polymer having anionic groups of 25-60 mol% and having a molecular weight of one hundred thousand to one million (Laid-open Japanese Patent Application No. Sho 60-185900), one in which cationic starch and anionic colloidal silica are used (Laid-open 30 Japanese Patent Application No. Sho 57-51900), one in which an acrylamide-based polymer having cationic groups and colloidal silica are used (Laid-open Japanese Patent Application No. Sho 62-15391), one in which colloidal silicic acid, cationic or amphoteric polyacrylamide derivative and cationic starch are added (Laid-open Japanese Patent Application No. Sho 62-110998), one in which a cationic polymer and bentonite are used to improve retention (Laid-open 35 Japanese Patent Application No. Sho 62-191598). In addition, there are known methods, one in which firstly a cationic polymer having a high molecular weight is added to cellulose slurry of paper stuff and secondly an anionic polymer having a middle molecular weight is added (Laid-open Japanese Patent Application No. Hei 4-245998), one in which a mixture of an anionic polymeric substance and bentonite is added to paper stuff after a cationic polymer flocculant is added (Laid-open Japanese Patent Application No. Sho 64-61588) and the like.

40 Although these methods improve retention or drainage property more than a method in which a water-soluble polymer is used alone, they are not satisfactory because of the worsening situation of paper stuff, deterioration in the quality of water for papermaking and the like caused by recent progress in the papermaking technology and increased use of recycled pulp. Therefore, a method for further improving retention or drainage property is strongly desired.

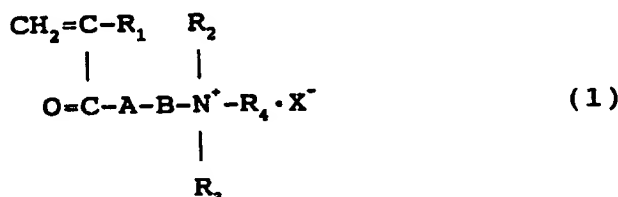
It is therefore a object of the present invention to improve productivity in papermaking and drying steps by improving the yields of cellulose fibers, fillers and the like and/or drainage property in the papermaking process. More specifically, it is an object of the present invention to produce high-quality paper by making uniform a composition distribution 45 in the direction of the thickness of a paper layer, to reduce cost by preventing the effluence of paper stuff and fillers, and not to reduce the papermaking speed even when paper is produced from pulp having a high beating degree. Another object of the present invention is to establish a stable papermaking method by keeping circulating white water clean by improving retention and/or drainage property. A further object of the present invention is to provide a papermaking method which is intended to reduce a load in a white water recovery step and a load in a waste water treatment step by 50 improving retention and/or drainage property.

DISCLOSURE OF THE INVENTION

55 The inventors of the present invention have conducted intensive studies to attain the above objects and have found that the above objects can be attained by a papermaking method for improving retention and/or drainage property by adding a ionic water-soluble polymer obtained by the following dispersion polymerization method to paper stuff and mixing them, and then adding and mixing an anionic additive selected from the group consisting of anionic colloidal silica,

anionic (co)polymer, bentonite and a mixture thereof in the papermaking step. The present invention has been predicated upon this finding.

The dispersion polymerization method for the ionic water-soluble polymer used in the present invention is a polymerization method for obtaining a dispersion of fine polymer particles by polymerizing (A) 3 to 100 mol% of a water-soluble cationic vinyl monomer represented by the following formula (1) or a mixture thereof, (B) 0 to 30 mol% of a water-soluble anionic vinyl monomer and (C) the remainder consisting of a water-soluble nonionic vinyl monomer, based on the total of all the monomers, under agitation in a aqueous salt solution capable of dissolving the monomers but not the produced polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous salt solution.



(wherein A is O or NH; B is C₂H₄, C₃H₆ or C₃H₅OH; R₁ is H or CH₃; R₂ and R₃ are each CH₃ or C₂H₅; R₄ is H, CH₃, C₂H₅ or benzyl group; and X⁻ is a anionic counter ion.)

In other words, the present invention is a papermaking method comprising the steps of adding to paper stuff in a papermaking step a ionic water-soluble polymer produced by a polymerization method called dispersion polymerization for obtaining a dispersion of fine polymer particles by polymerizing specific water-soluble ionic vinyl monomers under agitation in a aqueous salt solution capable of dissolving the monomers but not the produced polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous salt solution, and then adding an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof so as to improve retention and/or drainage property.

The present invention further provides a papermaking method in which a salt forming the aqueous salt solution used in the production of the ionic polymer used in the above method is a divalent anionic salt.

The present invention further provides a papermaking method in which the dispersant used in the production of the ionic polymer used in the above method is a cationic polymer electrolyte obtained by polymerizing 50 to 100 mol% of at least one cationic monomer selected from salts of dimethylaminoethylacrylate, salts of dimethylaminoethylmethacrylate, salts of dimethylaminopropylacrylamide, salts of dimethylaminopropylmethacrylamide, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, dimethyldiallylammonium chloride and mixtures thereof, and 0 to 50 mol% of acrylamide.

The present invention further provides a papermaking method in which the intrinsic viscosity of the ionic water-solution polymer in a 2 wt% ammonium sulfate aqueous solution is 5 dl/g to 30 dl/g in the above method.

The present invention further provides a papermaking method in which the ionic water-soluble polymer is added in an amount of 0.001 to 0.2 wt% of the suspended substance of the paper stuff (called as "paper stuff SS") and the anionic additive is added in a total amount of 0.001 to 0.5 wt% of the paper stuff SS. In this instance, the ionic polymer is preferably added in an amount of 0.001 to 0.05 wt% and the anionic additive is preferably added in a total amount of 0.01 to 0.2 wt%.

The present invention still further provides a papermaking method in which the anionic additive, which is added after the ionic polymer is added and mixed, is anionic (co)polymer comprising acrylic acid of 15~100 mol% and acrylamide of 0~85 mol% based on the total of all the monomers.

The present invention still further provides a papermaking method in which the anionic additive, which is added after the ionic polymer is added and mixed, is anionic (co)polymer polymerized in a aqueous salt solution capable of dissolving the monomers but not the produced polymer, and a water-diluted dispersion of the resulted polymer fine particles is added thereto as said anionic additive.

The present invention further provides a papermaking method in which the ionic water-soluble polymer is added prior to the centrifugal screening of the papermaking process and the anionic additive is added after the centrifugal screening in the above method.

The present invention is a papermaking method in which the ionic water-soluble polymer contains a water-soluble anionic vinyl monomer in an amount of 1 to 30 mol% of the total of all the monomers in the above method. In this instance, the anionic monomer is preferably at least one selected from acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, acrylamide-2-methylpropanesulfonic acid and salts thereof, and mix-

tures thereof, the most preferably acrylic acid.

The present invention is a papermaking method in which the gram equivalent of the water-soluble cationic vinyl monomer used in the ionic water-soluble polymer is greater than the gram equivalent of the water-soluble anionic vinyl monomer in the above method.

The present invention provides a papermaking method in which the ionic water-soluble polymer does not contain a water-soluble anionic vinyl monomer in the above method.

The present invention further provides a papermaking method in which the water-soluble nonionic vinyl monomer is acrylamide in the above method.

The present invention further provides a papermaking method in which the water-soluble cationic vinyl monomer is a tertiary salt and/or quaternary product of dimethylaminoethylacrylate in the above method.

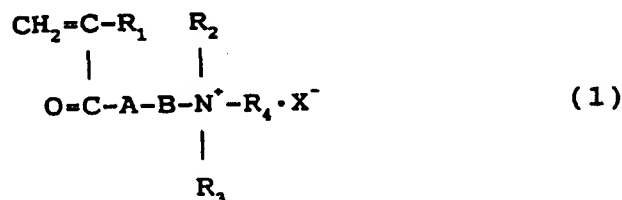
BEST MODE FOR CARRYING OUT THE INVENTION

A method for producing an ionic water-soluble polymer used in the present invention is dispersion polymerization for obtaining a dispersion of the ionic water-soluble polymer by polymerizing water-soluble ionic vinyl monomers under agitation in an aqueous salt solution capable of dissolving the monomers used but not the produced ionic water-soluble polymer in the presence of a dispersant composed of a polymer electrolyte soluble in the aqueous solution. This method is disclosed in European Patent Publication No. 183466, European Patent Publication No. 364175 and the like.

The inventors of the present invention have found that, when the ionic water-soluble polymer produced by dispersion polymerization in an aqueous salt solution is used in combination with an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof, it greatly improves retention and/or drainage property, compared with an ionic water-soluble polymer having the same monomer composition and produced by a conventional polymerization method such as polymerization in an aqueous solution or water-in-oil type emulsion polymerization. The present invention is predicated upon this finding.

This is considered to be caused by the characteristic feature of the dispersion polymerization in an aqueous salt solution. In this polymerization method, the monomers are uniformly dissolved in the aqueous salt solution, which is a polymerization solvent, before polymerization. However, as the polymerization proceeds, the produced polymer separates out from the aqueous salt solution and forms a dispersion of fine particles with the aid of a dispersant. That is, phase separation from a uniform phase to double phases takes place. Although this polymerization mechanism has not been elucidated yet, it is assumed that a polymer having a specific molecular structure, such as a branched polymer or block copolymer, is produced unlike polymerization in an aqueous solution or water-in-oil type emulsion polymerization in which polymerization is carried out in a uniform phase. It can be considered that this specific molecular structure is a primary factor of improving retention and/or drainage property.

The water-soluble cationic vinyl monomer constituting the ionic water-soluble polymer used in the present invention is represented by the following formula (1):



(wherein A is O or NH; B is C₂H₄, C₃H₆ or C₃H₅OH; R₁ is H or CH₃; R₂ and R₃ are each CH₃ or C₂H₅; R₄ is H, CH₃, C₂H₅ or benzyl group; and X⁻ is an anionic counter ion.).

Preferred examples of the water-soluble cationic vinyl monomer represented by the above formula (1) include tertiary salts and/or quaternary products of dimethylaminoethylacrylate and dimethylaminoethylmethacrylate, and tertiary salts and/or quaternary products of dimethylaminopropylacrylamide and dimethylaminopropylmethacrylamide.

Typical examples of the tertiary salt include hydrochlorides and sulfates of the above monomers and typical examples of the quaternary product include methylated, ethylated and benzylated products of the above monomers.

Illustrative examples of the water-soluble cationic vinyl monomer represented by the above formula (1) include acryloyloxyethyltrimethylbenzylammonium chloride, methacryloyloxyethyltrimethylbenzylammonium chloride, acrylamidepropyltrimethylbenzylammonium chloride, methacrylamidepropyltrimethylbenzylammonium chloride, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, hydrochloride salt or sulfuric acid salt of dimethylaminoethylacrylate, hydrochloride salt or sulfuric acid salt of dimethylaminoethylmethacrylate, hydrochloride

salt or sulfuric acid salt of dimethylaminopropylacrylamide, hydrochloride salt or sulfuric acid salt of dimethylaminopropylmethacrylamide, and the like. Out of these, particularly preferred water-soluble cationic vinyl monomer as a monomer containing a benzyl group is acryloyloxyethyltrimethylbenzylammonium chloride and preferred water-soluble cationic vinyl monomer as a monomer containing no benzyl group is acryloyloxyethyltrimethylammonium chloride.

Examples of the water-soluble anionic vinyl monomer used in the present invention include, for example, itaconic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, acrylic and methacrylic anionic monomers, and mixtures thereof.

Typical acrylic and methacrylic anionic monomers include acrylic acid, methacrylic acid and salts thereof, 2-acrylamide-2-methylpropanesulfonic acid and salts thereof, and mixtures thereof. Out of these, preferred water-soluble anionic vinyl monomers are acrylic acid and methacrylic acid, and the most preferred is acrylic acid.

Examples of the water-soluble nonionic vinyl monomer used in the ionic water-soluble polymer of the present invention include, for example, acrylamide, methacrylamide, hydroxyethylacrylate, hydroxyethylmethacrylate and the like. From a view point of improving retention and/or drainage property as a chemical for papermaking, acrylamide is the most preferred.

The ionic water-soluble polymer used in the present invention is obtained by polymerizing (A) 3 to 100 mol% of a water-soluble cationic vinyl monomer represented by the above formula (1), (B) 0 to 30 mol% of a water-soluble anionic vinyl monomer and (C) the remainder consisting of a water-soluble nonionic vinyl monomer based on the total of all the monomers.

The above ionic water-soluble polymer used in the present invention is preferably a cationic or amphoteric water-soluble polymer. As an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof is anionic, use of an anionic or nonionic water-soluble polymer is not preferred as a polymer to be first added.

When the above ionic water-soluble polymer is a cationic water-soluble polymer, out of the vinyl monomers represented by the above formula (1), a homopolymer of a water-soluble cationic vinyl monomer containing a benzyl group, or a copolymer of a plurality of vinyl monomers represented by the above formula (1) or a copolymer thereof further comprising a water-soluble nonionic vinyl monomer such as acrylamide or methacrylamide is preferred. Although a preferred molar ratio of these monomers is not particularly limited, such a molar ratio is essential that the aqueous salt solution serving as a polymerization solvent does not dissolve the produced ionic water-soluble polymer or salts out the produced ionic water-soluble polymer.

For example, a preferred range of the molar ratio is such that a polymer comprising 3 to 100 mol% of a water-soluble cationic vinyl monomer containing a benzyl group and represented by the above formula (1) or a mixture thereof, 0 to 50 mol% of another water-soluble cationic vinyl monomer containing no benzyl group and represented by the above formula (1) or a mixture thereof, and the remainder consisting of a nonionic monomer is salted out.

The monomer containing a benzyl group which is the water-soluble cationic vinyl monomer of the above formula (1) has an amino group bonded to the very hydrophobic benzyl group. As a result, the produced polymer hardly dissolves in the aqueous salt solution though it is a water-soluble polymer. Therefore, when the cationic water-soluble polymer contains a benzyl group-containing water-soluble cationic vinyl monomer of the above formula (1) as a constituent element, a molar ratio of the monomer to another water-soluble cationic vinyl monomer of the above formula (1) having no benzyl group can be set to a wide range.

Meanwhile, when the cationic water-soluble polymer contains a water-soluble cationic vinyl monomer represented by the above formula (1) and having no benzyl group as a constituent element, the molar ratio of the water-soluble cationic vinyl monomer to acrylamide or methacrylamide is preferably in the range of 3:97 to 30:70.

The amphoteric water-soluble polymer as the ionic water-soluble polymer used in the present invention is preferably a copolymer comprising 3 to 99 mol% of a water-soluble cationic vinyl monomer represented by the above formula (1) or a mixture thereof, 1 to 30 mol% of the above water-soluble anionic vinyl monomer, and the remainder consisting of a water-soluble nonionic vinyl monomer such as acrylamide or methacrylamide. Although a preferred molar ratio of these monomers is not particularly limited, such a molar ratio is essential that the aqueous salt solution serving as a polymerization solvent does not dissolve the produced polymer or salts out the produced polymer.

However, in order to make the amphoteric water-soluble polymer remarkably show its characteristic features, all the ionic vinyl monomers, both cationic and anionic, are preferably contained in the copolymer in an amount of 5 mol% or more, more preferably 10 mol% or more. When all the ionic vinyl monomers are contained in the copolymer in a amount of less than 5 mol%, retention, drainage and other properties will be unsatisfactory.

As for the molar ratio of each ionic vinyl monomer, the gram equivalent of the water-soluble cationic vinyl monomer is preferably greater than the gram equivalent of the water-soluble anionic vinyl monomer because it is preferred that the amphoteric copolymer contains more cationic groups than anionic groups. Particularly preferably, the gram equivalent value of the cationic groups is at least two times or more the gram equivalent value of the anionic groups.

A more preferred example of the above amphoteric water-soluble polymer is a dispersion copolymer comprising 3 to 99 mol% of a water-soluble cationic vinyl monomer containing a benzyl group, out of water-soluble cationic vinyl mon-

omers represented by the above formula (1), or a mixture thereof, 0 to 50 mol% of another water-soluble cationic vinyl monomer represented by the above formula (1) or a mixture thereof, 1 to 30 mol% of the above water-soluble anionic vinyl monomer and the remainder consisting of acrylamide.

Another preferred example of the above amphoteric water-soluble polymer is a dispersion copolymer comprising 3 to 30 mol% of a water-soluble cationic vinyl monomer containing no benzyl group and represented by the above formula (1), 1 to 30 mol% of an anionic monomer and the remainder consisting of acrylamide.

Further, monomers other than the above monomers, for example, hydrophobic monomers such as acrylonitrile, methylacrylate, ethylacrylate, 2-ethylhexylacrylate and styrene may be copolymerized if the produced copolymer is water-soluble.

Polymerization is carried out in the presence of a dispersant while a plurality of monomers are stirred in an aqueous salt solution. The total concentration of the monomers at this point is preferably 5 wt% or more, more preferably 10 wt% or more, the most preferably 15 to 40 wt%. When the total concentration of the monomers is less than 5 wt%, the concentration of the polymer in the aqueous dispersion becomes low and thus it is economically disadvantageous.

It is an essential requirement that the aqueous salt solution which serves as a polymerization solvent and dispersion medium used in the present invention at the time of producing a polymer should not dissolve the produced polymer or should salt out the produced polymer. That is, a combination of the composition of the monomers of the ionic water-soluble polymer and the type and concentration of the salt that satisfies this condition is essential.

The salt used in the aqueous salt solution is preferably a polyvalent anionic salt. Typical examples of the salt include sodium sulfate, ammonium sulfate, magnesium sulfate, aluminum sulfate, disodium hydrogen phosphate and the like. Other salts may be used if the aqueous salt solutions thereof dissolve the monomers and the dispersant and do not dissolve the produced polymer. Out of these, sulfates are preferred. In terms of valence, divalent anionic salts are preferred. More specifically, ammonium sulfate and sodium sulfate are the most preferred.

The concentration of the salt in a reaction solution during the polymerization process vary depending on the molar ratio of the water-soluble cationic vinyl monomer represented by the above formula (1), the molar ratio of the water-soluble anionic vinyl monomer and the type of the salt used, and hence, is not particularly limited.

However, the concentration of the salt in the reaction solution during the polymerization process is preferably between 15 wt% based on the polymerization solvent obtained by subtracting the weight of the monomers from the weight of the polymerization reaction solution and the saturation concentration, or between 15 wt% and the limit of solubility, more preferably between 15 wt% and 30 wt%, the most preferably between 15 wt% and 25 wt%. If the concentration of the salt is less than 15 wt%, the viscosity of the reaction solution under reaction becomes too high to make it difficult to successfully complete the polymerization process.

Although a salt is added to a solvent at the time of polymerization, part of the salt may alternatively be added to the dispersion after the completion of polymerization. The viscosity of the dispersion can be made lower when part of the salt is added to the dispersion after the completion of the polymerization process than that when the salt is all added to the solvent at the time of polymerization. The concentration of the salt in the dispersion obtained by adding part of it to the dispersion after the completion of the polymerization process is preferably between 15 wt% and the saturated concentration or between 15 wt% and the limit of solubility, more preferably between 15 wt% and 25 wt%.

Any combination of the composition of monomers in which a produced polymer is not salted out even by changing the type of the salt or the concentration of the salt or the composition of monomers of an ionic water-soluble polymer in which the salting-out of a produced polymer does not occur and the type and concentration of the salt is out of the scope of the present invention.

It is an essential requirement that the dispersant composed of a polymer electrolyte which is present at the time of polymerization is soluble in the aqueous salt solution.

A cationic polymer electrolyte is preferably used as the polymer electrolyte because a cationic polymer is preferred as an ionic polymer which is the product and the gram equivalent value of the cationic monomer contained in the amphoteric polymer is preferably greater than the gram equivalent value of the anionic monomer contained therein. The dispersant is more preferably a cationic polymer electrolyte obtained by polymerizing 50 to 100 mol% of at least one cationic monomer selected from salts of dimethylaminoethylacrylate, salts of dimethylaminoethylmethacrylate, salts of dimethylaminopropylacrylamide, salts of dimethylaminopropylmethacrylamide, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, dimethyldiallylammonium chloride and mixtures thereof, and 50 to 0 mol% of acrylamide.

The amount of the polymer electrolyte dispersant is about 1 to 15 wt%, preferably about 1 to 10 wt%, based on the total weight of all the monomers. If the amount is less than 1 wt%, the produced polymer cannot be obtained in a dispersed state and undesirably agglomerates to a large mass. If the amount is more than 15 wt%, the viscosity of the finally obtained dispersion is undesirably too high to lose easy flowability.

In the present invention, the polymerization process can be initiated by any known method if the resulting polymer can be obtained in the form of a dispersion. However, it is preferable to use a polymerization initiator therefor. There are

no limitations to the selection of a polymerization initiator, but generally a free-radical initiator may be preferably used. The polymerization initiator may preferably be selected from those of a redox type, those of an azo type and those of any other types. Examples of the redox type initiator include combinations of one selected from ammonium peroxosulfate, potassium peroxodisulfate, hydrogen peroxide, and benzoyl peroxide, and one selected from sodium hydrogen sulfite, ferrous sulfate, tetramethylethylenediamine, and dimethylaniline. Examples of the azo type initiator include

2,2'-azobis(2-amidinopropane)dihydrochloride,
2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 2,2'-azobisisobutyronitrile,
2,2'-azobis(2,4-dimethylvaleronitrile), and
2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile). Examples of the other type initiator include ammonium peroxosulfate,

potassium peroxodisulfate, hydrogen peroxide, acetyl peroxide, lauroyl peroxide, benzoyl peroxide, cumene hydroperoxide, di-tert-butyl peroxide, tetramethylthiuram disulfide, dibenzoyldisulfide, and p-toluenesulphonic acid.

In addition, for the purpose of the present invention, there are no specific limitations to the polymerization temperature so far as the polymerization initiator works properly at the selected temperature. As for the type of the polymerization initiator,

2,2'-azobis(2-amidinopropane)dihydrochloride,
2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride and the like are preferred because they are water-soluble, easily handled and controllable.

The polymer dispersion contains the ionic water-soluble polymer at a high concentration equal to or higher than 5 wt%, normally at a level between 5 wt% and about 40 wt%. The dispersion contains the above salt and above dispersant.

While the dispersion contains an ionic water-soluble polymer at a high concentration, its viscosity is normally as low as 10 to 3000 mPa · S because the ionic water-soluble polymer is stably dispersed in the aqueous salt solution in the form of fine particles. Thus, it is easily flowable and extremely easy to be handled.

The average particle diameter of the particles of the ionic water-soluble polymer in the above dispersion is normally 0.1 to 150 μm , preferably 0.1 to 50 μm , more preferably 0.1 to 30 μm . If the average particle diameter of the particles of the ionic water-soluble polymer exceeds 150 μm , they can easily precipitate to damage the stable storability of the dispersion and require a long time before they are completely dissolved into water because of low solubility due to the large sizes of the particles of the ionic water-soluble polymer if the dispersion is mixed with water for use.

There are no specific limitations to the molecular weight of the ionic water-soluble polymer in the above dispersion. However, it preferably has a large molecular weight when it is used in a papermaking process. When the dispersion of the ionic water-soluble polymer is dissolved in a 2 wt% aqueous solution of ammonium sulfate, the intrinsic viscosity of the polymer is normally found within a range of 5 dl/g to 30 dl/g. If the intrinsic viscosity is less than 5 dl/g, the effect of improving retention and/or drainage property will be insufficient and if the intrinsic viscosity is more than 30 dl/g, the formation of paper will become worse, giving an ill effect on the quality of the produced paper.

The above dispersion is stably storable and is free from the problem of agglomerating to a large mass even if stored at room temperature.

In the present invention, the anionic additive is one selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof.

The anionic colloidal silica used in the present invention is produced by maintaining an aqueous solution of sodium orthosilicate at a pH value of 1 to 4 and a commercial product can be used. The anionic colloidal silica is generally a silicon dioxide having an OH group on the surface by hydration in water and a porous particle surface generally charged with negative (-) electricity in water. More specifically, the anionic colloidal silica is a colloidal silicic acid sol having a surface area of about 50 to about 1,000 m^2/g , preferably about 300 to about 700 m^2/g or colloidal silica containing about 20 to 90 % of this colloidal silicic acid sol as disclosed in Laid-open Japanese Patent Application No. Sho 57-51900. Long and narrow anionic silica sol having a particle diameter measured by a dynamic light scattering method of about 40 to 300 nm and an uniform thickness of about 5 to 20 nm, and showing extension on the same plane is preferably used.

As the bentonite, a commercial product can be used.

The anionic (co)polymer used in the present invention is a polymer or a copolymer comprising anionic monomers of which structure includes an anionic group. Examples of the anionic monomer are preferably one selected from acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, maleic acid and salts thereof, fumaric acid and salts thereof, acrylamide-2-methylpropanesulfonic acid and salts thereof, and a mixture thereof. The most preferred anionic monomer is acrylic acid, namely, the anionic (co)polymer is preferably an acrylic acid (co)polymer. In addition to the above monomers, other monomers can be copolymerized i.e., nonionic monomer, e.g., methacrylamide, acrylonitrile, methacrylonitrile, methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, hydroxyethylacrylate, hydroxyethylmethacrylate, and the like.

It is preferred that the acrylic acid (co)polymer comprises acrylic acid of 15~100 mol% and acrylamide of 0~85 mol% based on the total of all the monomers.

In the present invention the preparative method of the used anionic (co)polymer should not be limited, and thus any known methods can be applied. Out of them, polymerizing methods for obtaining fine polymer particles by polymerizing in an aqueous salt solution capable of dissolving the monomers but not the produced polymer is preferred.

The prepared anionic (co)polymer preferably has a molecular weight of 1.5 million or more. The prepared polymer is added to paper stuff as a water-diluted dispersion of the resulted polymer fine particles.

In the papermaking step, the dosage of the ionic water-soluble polymer is preferably 0.001 to 0.2 wt% based on the weight of the paper stuff SS, and the total dosage of the anionic additive is preferably 0.001 to 0.5 wt% based on the weight of the paper stuff SS.

Further, the dosage of the ionic water-soluble polymer is more preferably 0.001 to 0.05 wt% based on the weight of the paper stuff SS and the total dosage of the anionic additive is more preferably 0.01 to 0.2 wt% based on the weight of the paper stuff SS.

When the dosage of the chemical(s) is too small, the effect is reduced and when the dosage is too large, waste materials on felt or wires used in the papermaking step is liable to occur.

In the papermaking method of the present invention, the time for adding each additive is not particularly limited.

However, the ionic water-soluble polymer needs to be first added, followed by an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof. Preferably, in the papermaking step, the ionic water-soluble polymer is added before the centrifugal screening of the papermaking process and the anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof is added after the centrifugal screening.

After the addition of the ionic water-soluble polymer, it is preferred that the polymer is uniformly distributed to the surface of a suspended substance by suitable shearing. After the addition of the anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof, it is desirable to prevent the destruction of an agglomerate caused by mixing excessively.

According to the present invention, the ionic water-soluble polymer produced by dispersion polymerization in an aqueous salt solution greatly improves retention and/or drainage property when used in combination with an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof, compared with an ionic water-soluble polymer having the same monomer composition and produced by a conventional polymerization method such as aqueous solution polymerization or water-in-oil type emulsion polymerization.

As described above, according to dispersion polymerization in an aqueous salt solution, as polymerization proceeds, the produced polymer separates out from the aqueous salt solution which serves as a polymerization solvent. Therefore, a specific molecular structured polymer such as branched polymer is produced unlike polymerization which is carried out in a uniform phase, and this specific molecular structure is assumed to be the primary factor of improving retention and/or drainage property.

EXAMPLES

The present invention will be described in greater detail by way of examples hereinafter, although the scope of the present invention is by no way limited by the following examples.

(Preparation Examples of Ionic Polymer)

(Nos. 1 to 6)

4.2 g of polyacryloyloxyethyltrimethylammonium chloride as a dispersant and 84.0 g of ammonium sulfate as a separating agent were dissolved in 303.0 g of ion exchanged water in a 1-liter five-necked separable flask equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet. 100.0 g of each of monomers having respective compositions shown in Table 1 was charged into the flask, followed by heating them to 50°C and the air inside was displaced with nitrogen. 2.0 g of a 1 % aqueous solution of 2,2'-azobis(2-amidinopropane)dihydrochloride was further added thereto as a polymerization initiator and the polymerization operation was conducted with stirring at 50°C for 10 hours to obtain a polymer in the form of fine particles dispersed in an aqueous salt solution. To this reaction mixture was added 21 g of ammonium sulfate to obtain dispersed polymer samples A to F to be used in the present invention.

The monomer compositions and intrinsic viscosities in a 2 wt% aqueous solution of ammonium sulfate of the dispersed polymer samples A to F are shown in Table 1.

(Nos. 7 to 12)

For comparison, monomers having respective compositions shown in Table 1 were used to obtain comparative samples a to f by aqueous solution polymerization and reverse-phase emulsion polymerization similarly.

The monomer compositions and intrinsic viscosities in the 2 wt% aqueous solution of ammonium sulfate of the comparative samples a to f are shown in Table 1.

Table 1

No.	Ionic Polymer Sample	Monomer Composition Ratio (mol%)				Intrinsic Viscosity (dl/g)	Polymerization Method
		ABC	DMQ	AAc	AAM		
1	A	15	0	0	85	5.8	(1)
2	a	0	10	0	90	6.2	(1)
3	C	15	0	5	80	13.6	(1)
4	D	10	10	10	70	14.6	(1)
5	E	40	20	0	40	7.8	(1)
6	F	40	20	20	20	12.4	(1)
7	a	15	0	0	85	7.2	(2)
8	b	0	10	0	90	6.3	(2)
9	c	15	0	5	80	14.0	(2)
10	d	10	10	10	70	14.6	(2)
11	e	40	20	0	40	7.8	(3)
12	f	40	20	20	20	13.8	(3)

* ABC: acryloyloxyethyltrimethylbenzylammonium chloride
 DMQ: acryloyloxyethyltrimethylammonium chloride
 AAc: acrylic acid
 AAm: acrylamide
 (1): Dispersion polymerization
 (2): Aqueous solution polymerization
 (3): Reverse-phase emulsion polymerization

(Preparation of Acrylic (Co)Polymer)

96 g of a 50 wt% aqueous solution of acrylamide, 12 g of acrylic acid and 46.5 g of sodium sulfate were dissolved in 145.5 g of ion exchanged water in a 500-milliliter five-necked separable flask equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen inlet, followed by heating them to 25°C by means of a water bath and the air inside was displaced with nitrogen while stirring for 30 minutes. 0.6 ml of a 10 wt% aqueous solution of ammonium persulfate and 0.6 ml of a 10 wt% aqueous solution of sodium hydrosulfite were added thereto as a polymerization initiator and the polymerization operation was conducted with stirring. After 2 minutes, the solution was whitened. At this time, the water bath was removed and the temperature inside was about 70°C after 30 minutes by the heat of polymerization. After then, the polymerization temperature was maintained by a 70°C water bath for 2 hours and the polymerization reaction was completed.

The prepared acrylic acid-acrylamide copolymer had a viscosity of 320 mPa · S measured by a Brooke-field viscometer. According to the microscopic investigation, an average diameter of the prepared copolymer particles was 5 µm and thus the resulted polymer was obtained in a form of a dispersion. The prepared dispersion (20 wt% polymer concentration) was diluted by ion exchanged water into 1/40 concentration and the viscosity of the diluted dispersion was 3.0 mPa · S measured by a Brooke-field viscometer where the polymer was not dissolved. The polymer was neutralized by sodium hydroxide and the intrinsic viscosity in 1N sodium chloride aqueous solution was 6.0 dl/g. The prepared acrylic acid-acrylamide copolymer dispersion is designated as sample G.

A dispersion of homopolymer of acrylic acid was prepared by the same preparative method as above. The dispersion is designated as sample H. The intrinsic viscosity of the sample H in 1N sodium chloride aqueous solution is 6.1 dl/g.

(Examples 1 to 14)

A retention test was conducted by adding the ionic polymer dispersions (A) to (F) to paper stuff.

15 wt% (based on the weight of pulp) of ground calcium carbonate was added as a filler to bleached kraft pulp of
5 broad-leaved tree (L-BKP) [Canadian standard freeness (C.S.F) = 330] to adjust the concentration of SS to 0.5 wt%.

Using this slurry, the retention rate was measured by a Britt-type dynamic jar tester.

The test was conducted in the following procedure.

500 ml of 0.5 wt% paper stuff was put into the Britt-type dynamic jar tester.

10 Stirring was started at 1,500 rpm and a 0.1 wt% aqueous solution of each of the cationic polymers obtained in the above preparation examples was added. At this point, time counting was started.

After 30 seconds, 0.1 wt% bentonite (trade name: Organosob-O, manufactured by Allied Colloid Co.) and/or 0.1 wt% anionic colloidal silica (trade name: BMA-780, manufactured by Nissan Ekanobel Co.) were/was added.

After another 30 seconds, a white water sampling cock was opened to flow in white water which has passed through a wire of 150 mesh.

15 The white water was thrown away for the initial 10 seconds and then collected for the succeeding 30 seconds. The amount of the white water during this time is represented by X (ml).

The white water was filtered by a quantization filter paper (No. 5C of Toyo Filter Co.) which has a dry weight of W_0 (g) at 105°C, dried at 105°C and measured for its weight. This weight is represented by W_1 (g).

20 Thereafter, the white water with the quantization filter paper was incinerated at 600°C and the weight of the ash content of the white water was measured. This weight is represented by f(g).

The SS concentration and the ash concentration of the white water are obtained from the following equations.

$$\text{SS concentration of white water (wt\%)} = \frac{W_1 - W_0}{X} \times 100 = \text{SS}_1$$

$$\text{ash concentration of white water (wt\%)} = \frac{f}{X} \times 100 = \text{Ash}_1$$

30 The SS concentration and the ash concentration were also measured for 0.5 wt% paper stuff. They are represented by SS_0 and Ash_0 , respectively.

The total one pass retention and filler one pass retention were calculated from the following equations.

$$\text{total one pass retention (T-OPR\%)} = \frac{\text{SS}_0 - \text{SS}_1}{\text{SS}_0} \times 100$$

$$\text{filler one pass retention (F-OPR\%)} = \frac{\text{Ash}_0 - \text{Ash}_1}{\text{Ash}_0} \times 100$$

The obtained results are shown in Table 2.

Table 2

Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt) (ppm)				
1	A	200	300	0	80.6	60.8
2	B	200	300	0	81.2	63.8
3	C	200	300	0	79.9	59.6
4	D	200	300	0	81.3	64.3

Table 2 (continued)

Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt) (ppm)				
9	E	200	300	0	80.8	62.1
6	F	200	300	0	79.5	58.8
7	A	300	0	500	82.5	63.9
9	B	300	0	500	83.2	66.1
9	C	300	0	500	81.5	62.1
10	D	300	0	500	83.2	67.9
11	E	300	0	500	82.5	63.2
12	F	300	0	500	81.6	61.1
13	A	300	150	250	83.4	68.7
14	D	300	150	250	83.6	69.9

(Comparative Examples 1 to 14)

The retention rate was measured in the same manner as in Examples 1 to 14 using solution polymerization type polymers and emulsion type polymers (a) to (f) in place of the polymer dispersions (A) to (F) used in Examples 1~14. The obtained results are shown in Table 3. The compositions and properties of the polymers are shown in Table 1.

Table 3

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on weight of SS) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on weight of SS) (ppm)				
1	a	200	300	0	78.3	49.5
2	b	200	300	0	77.3	42.3
3	c	200	300	0	78.0	53.0
4	d	200	300	0	76.5	41.2
5	e	200	300	0	77.7	47.8
6	f	200	300	0	76.5	40.4
7	a	300	0	500	79.3	53.3
6	b	300	0	500	78.4	48.3
9	c	300	0	500	78.6	54.9
10	d	300	0	500	78.5	43.9
11	e	300	0	500	79.3	51.4
12	f	300	0	500	78.5	45.1

Table 3 (continued)

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on weight of SS) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on weight of SS) (ppm)				
13	a	300	150	250	79.3	56.9
14	d	300	150	250	78.9	47.5

(Examples 15 to 30)

The retention rate was measured in the same manner as in Examples 1 to 14 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite. The obtained results are shown in Table 4.

Table 4

Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt) (ppm)					
15	A	250	0	150	0	81.8	62.2
16	B	250	0	150	0	82.0	62.0
17	C	250	0	150	0	82.4	62.5
18	D	250	0	150	0	82.5	62.5
19	E	250	0	150	0	82.3	62.2
20	F	250	0	150	0	82.1	62.0
21	A	250	0	0	150	82.3	62.0
22	B	250	0	0	150	82.5	62.5
23	C	250	0	0	150	82.5	62.5
24	D	250	0	0	150	82.3	62.2
25	E	250	0	0	150	82.1	62.0
26	F	250	0	0	150	81.9	62.0
27	A	250	250	80	0	86.0	67.5
28	D	250	250	80	0	85.5	68.5
29	A	250	250	0	80	87.5	67.2
30	D	250	250	0	80	87.5	68.5

(Comparative Examples 15 to 30)

The retention rate was measured in the same manner as in Comparative Examples 1 to 14 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite. The obtained results

are shown in Table 5.

Table 5

Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	T-OPR (%)	F-OPR (%)
	Kind	Dosage (based on SS wt) (ppm)					
15	a	250	0	150	0	76.2	54.2
16	b	250	0	150	0	77.0	54.0
17	c	250	0	150	0	77.5	54.5
18	d	250	0	150	0	77.5	54.5
19	e	250	0	150	0	77.2	54.2
20	f	250	0	150	0	77.0	54.0
21	b	250	0	0	150	77.0	54.0
22	b	250	0	0	150	77.5	54.5
23	c	250	0	0	150	77.5	54.5
24	d	250	0	0	150	77.2	54.4
25	e	250	0	0	150	77.0	54.1
26	f	250	0	0	150	76.5	54.0
27	a	250	250	80	0	81.0	60.5
28	d	250	250	80	0	80.5	60.5
29	a	250	250	0	80	82.5	60.2
30	d	250	250	0	80	82.5	60.0

(Examples 31 to 44)

A drainage test was conducted by adding ionic polymer dispersions (A) to (F) to paper stuff.

Mixed pulp prepared from 90 % of recycled pulp from corrugated board and 10 % of recycled pulp from newspaper (C.S.F. = 300) was diluted to a pulp concentration of 1 wt%, to which 3 wt% of a liquid alum was added (based on the weight of pulp) to obtain a pH value of 5.8.

300 ml of this slurry was put into a 500-ml beaker and a 0.1 wt% aqueous solution of each of the polymers (A) to (F) obtained in preparation example Nos. 1-6 was added while stirring by a three-one motor at 600 rpm. After 30 seconds, 0.1 wt% anionic colloidal silica and/or 0.1 wt% bentonite were/was added thereto. After another 30 seconds, stirring was stopped and this slurry was transferred to a 1-liter measuring cylinder. City water was added to the slurry to adjust the total amount to 1 liter, the measuring cylinder was turned around three times for mixing, and the resulting slurry was put into a Canadian Standard freeness tester. In accordance with the procedure for the measurement of C.S.F., the amount of drainage coming out of a lateral pipe was measured.

The obtained results are shown in Table 6.

Table 6

Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)			
31	A	200	200	0	480
32	B	200	200	0	470
33	C	200	200	0	483
34	D	200	200	0	470
35	E	200	200	0	482
36	F	200	200	0	475
37	A	300	0	500	503
39	B	300	0	500	490
39	C	300	0	500	503
40	D	300	0	500	495
41	E	300	0	500	505
42	F	300	0	500	502
43	A	300	100	300	513
44	D	300	100	300	570

(Comparative Examples 31 to 44)

The amount of drainage was measured in the same manner as in Examples 31 to 44 using the ionic polymers (a) to (f) shown in Table 7 in place of the polymer dispersions (A) to (F) used in Examples 31 to 44. The obtained results are shown in Table 7.

Table 7

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)			
31	a	200	200	0	442
32	b	200	200	0	452
33	c	200	200	0	446
34	d	200	200	0	435
35	e	200	200	0	455
36	f	200	200	0	443
37	a	300	0	500	460
38	b	300	0	500	465

Table 7 (continued)

Comparative Example	Ionic Polymer		Dosage of Anionic Colloidal Silica (based on SS wt) (ppm)	Dosage of Bentonite (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)			
39	c	300	0	500	463
40	d	300	0	500	450
41	e	300	0	500	470
42	f	300	0	500	460
43	a	300	100	300	470
44	d	300	100	300	462

(Examples 45 to 60)

The amount of drainage was measured in the same manner as in Examples 31 to 44 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite used in Examples 31 to 44. The obtained results are shown in Table 8.

Table 8

Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) (based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based on SS wt) (ppm)				
45	A	250	0	150	0	478
46	B	250	0	150	0	472
47	C	250	0	150	0	482
48	D	250	0	150	0	478
49	E	250	0	150	0	480
50	F	250	0	150	0	472
51	A	250	0	0	150	476
52	B	250	0	0	150	474
53	C	250	0	0	150	480
54	D	250	0	0	150	480
55	E	250	0	0	150	478
56	F	250	0	0	150	474
57	A	250	250	80	0	513
58	D	250	250	80	0	505
59	A	250	250	0	80	514
60	D	250	250	0	80	506

(Comparative Examples 45 to 60)

The amount of drainage was measured in the same manner as in Comparative Examples 31 to 44 using acrylic acid (co)polymers (G) or (H) and/or bentonite in place of the anionic colloidal silica and/or bentonite used in Comparative Examples 31 to 44. The obtained results are shown in Table 9.

Table 9

Comparative Example	Ionic Polymer		Dosage of Bentonite (based on SS wt) (ppm)	Dosage of Sample (G) based on SS wt) (ppm)	Dosage of Sample (H) (based on SS wt) (ppm)	Amount of Drainage (ml)
	Kind	Dosage (based SS wt) (ppm)				
45	a	250	0	150	0	448
46	b	250	0	150	0	442
47	c	250	0	150	0	442
48	d	250	0	150	0	448
49	e	250	0	150	0	446
50	f	250	0	150	0	444
51	a	250	0	0	150	446
52	b	250	0	0	150	440
53	c	250	0	0	150	440
54	d	250	0	0	150	440
55	e	250	0	0	150	446
56	f	250	0	0	150	444
57	a	250	250	80	0	483
58	d	250	250	80	0	475
59	a	250	250	0	80	484
60	d	250	250	0	80	476

INDUSTRIAL APPLICABILITY

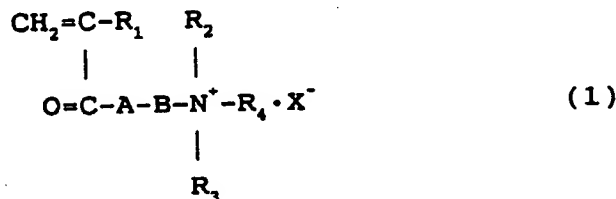
The papermaking method of the present invention makes it possible to improve the retention rates and/or drainage property of cellulose fibers and fillers in the papermaking process, whereby productivity in papermaking and drying steps can be improved. The papermaking method of the present invention also makes it possible to keep clean the circulating white water and reduce a load in the white water recovery step and a load in the waste water treatment step.

Claims

1. A papermaking method comprising the steps of:

adding to paper stuff in a papermaking step an ionic water-soluble polymer obtained by a polymerization method for obtaining a dispersion of fine polymer particles by polymerizing (A) 3 to 100 mol% of a water-soluble cationic vinyl monomer represented by the following formula (1) or a mixture thereof, (B) 0 to 30 mol% of a water-soluble anionic vinyl monomer, and (C) the remainder consisting of a water-soluble nonionic vinyl monomer based on the total amount of all the monomers under agitation in an aqueous salt solution capable of dissolving the monomers and not the produced polymer in the presence of a dispersant which is composed of a

polymer electrolyte soluble in the aqueous salt solution;
 mixing them; and
 adding and mixing an anionic additive selected from the group consisting of anionic colloidal silica, anionic (co)polymer, bentonite and a mixture thereof so as to improve retention and/or drainage property,



(wherein A is O or NH; B is C₂H₄, C₃H₆ or C₃H₅OH; R₁ is H or CH₃; R₂ and R₃ are each CH₃ or C₂H₅; R₄ is H, CH₃, C₂H₅ or benzyl group; and X⁻ is an anionic counter ion.).

2. The papermaking method according to claim 1, wherein a salt forming the aqueous salt solution is a divalent anionic salt.
3. The papermaking method according to claims 1 or 2, wherein said dispersant is a cationic polymer electrolyte obtained by polymerizing 50 to 100 mol% of a cationic monomer selected from salts of dimethylaminoethylacrylate, salts of dimethylaminoethylmethacrylate, salts of dimethylaminopropylacrylamide, salts of dimethylaminopropylmethacrylamide, acryloyloxyethyltrimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, acrylamidepropyltrimethylammonium chloride, methacrylamidepropyltrimethylammonium chloride, dimethyldiallylammonium chloride and mixtures thereof, and 0 to 50 mol% of acrylamide.
4. The papermaking method according to any one of claims 1 to 3, wherein said ionic water-soluble polymer has an intrinsic viscosity in a 2 wt% ammonium sulfate aqueous solution of 5 dl/g to 30 dl/g.
5. The papermaking method according to any one of claims 1 to 4, wherein the dosage of said ionic polymer is 0.001 to 0.2 wt% based on the weight of said paper stuff SS and the total dosage of said anionic additive is 0.001 to 0.5 wt% based on the weight of said paper stuff SS.
6. The papermaking method according to claim 5, wherein the dosage of said ionic polymer is 0.001 to 0.05 wt% based on the weight of said paper stuff SS and the total dosage of said anionic additive is 0.01 to 0.2 wt% based on said weight of the paper stuff.
7. The papermaking method according to any one of claims 1 to 6, wherein the anionic additive is an anionic (co)polymer comprising acrylic acid of 15~100 mol% and acrylamide of 0~85 mole % based on the total of all the monomers.
8. The papermaking method according to any one of claims 1 to 7, wherein the anionic additive, which is added after the ionic polymer is added and mixed, is an anionic (co)polymer polymerized in an aqueous salt solution capable of dissolving the monomers but not the produced polymer, and a water-diluted dispersion of the resulted polymer fine particles is added thereto as said anionic (co)polymer.
9. The papermaking method according to any one of claims 1 to 8, wherein said ionic water-soluble polymer is added before the centrifugal screening of the papermaking process and said anionic additive is added after the centrifugal screening.
10. The papermaking method according to any one of claims 1 to 9, wherein said ionic water-soluble polymer contains 1 to 30 mol% of said water-soluble anionic vinyl monomer based on the total of all the monomers.
11. The papermaking method according to claim 10, wherein said anionic monomer is one selected from acrylic acid and salts thereof, methacrylic acid and salts thereof, itaconic acid and salts thereof, acrylamide-2-methylpropanesulfonic acid and salts thereof, and mixtures thereof.

12. The papermaking method according to claim 11, wherein said anionic monomer is acrylic acid.

13. The papermaking method according to any one of claims 1 to 12, wherein the gram equivalent value of said water-soluble cationic vinyl monomer used in said ionic water-soluble polymer is greater than the gram equivalent value of said water-soluble anionic vinyl monomer.

14. The papermaking method according to any one of claims 1 to 9, wherein said ionic water-soluble polymer dose not contain any water-soluble anionic vinyl monomer.

15. The papermaking method according to any one of claims 1 to 14, wherein said water-soluble nonionic vinyl monomer is acrylamide.

16. The papermaking method according to any one of claims 1 to 15, wherein said water-soluble cationic vinyl monomer is a tertiary salt and/or quaternary product of dimethylaminoethylacrylate.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/03748

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ D21H17/45

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ D21H17/45

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-245998, A (Nalco Chemical Co.), September 2, 1992 (02. 09. 92) & UA, 5098520, A & EP, 497030, A1	1 - 16

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" documents defining the general state of the art which is not considered to be of particular relevance

"B" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"A" document member of the same patent family

Date of the actual completion of the international search

March 25, 1997 (25. 03. 97)

Date of mailing of the international search report

April 8, 1997 (08. 04. 97)

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